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MATHEMATICAL MODELING OF PHOTOCHEMICAL AIR POLLUTION

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Abstract

This paper summarizes the key elements of a project directed at developing a comprehensive mathematical model capable of describing the formation and transport of chemically reacting species in the turbulent planetary boundary layer. The model is intended for routine application in the design and evaluation of urban-scale air pollution control strategies. Some examples illustrating the use of the model in the South Coast Air Basin of Southern California are presented.

1. INTRODUCTION

A key component in the development of rational, economically efficient air pollution control strategies is a sound methodology for predicting the likely air quality impact of changes in emissions. When the national ambient air quality standards were set in 1971, relatively little had been done to develop photochemical oxidant* prediction relationships. A key question implicit in the legislation is: to what extent, in both an absolute and relative sense, should emissions of reactive hydrocarbons (RHC) and nitrogen oxides (NO_x) be controlled in order to achieve a desired level of oxidant air quality? The fact that oxidant air quality is nonlinearly related to precursor emissions of NO_x and RHC's considerably complicates the development of control strategies. The Environmental Protection Agency (EPA), faced with a pressing need, specified the so-called Appendix J rollback relationship as the only approved technique.[1] Although the method has been widely used, much concern has been expressed as to its adequacy.[2,3,4] In fact the Clean Air Amendments of 1977[5] include a number of provisions specifically calling for the use of improved dispersion models in the air quality planning process. This paper summarizes some of the results of a research program directed at developing advanced techniques for predicting oxidant air quality within an urban airshed.

2. MODEL FORMULATION

Within this paper, the means of relating contaminant emissions to resultant air quality, under specified meteorological conditions, will be referred to as an 'air quality model.' While a large variety of approaches have been proposed, varying in complexity from simple charts and formulae to complex numerical simulation, the

*In this paper photochemical oxidant air pollution refers primarily to ozone (O_3) and to a lesser extent peroxyacetyl nitrate (PAN) and nitrogen dioxide (NO_2).

various techniques can be divided into two basic classes. Models which are based on a fundamental description of the physics and chemistry of the atmospheric processes are classified as a priori approaches. Particular attention was given to the need for such models in the recent National Academy of Sciences report on Ozone and Other Photochemical Oxidants.[5] Those methods which employ empirical relationships deduced from observational data are known as a posteriori techniques. The fundamental weakness of the latter approaches is that they do not attempt to quantify, in an explicit manner, the underlying causal phenomena. A detailed evaluation of all the various techniques is beyond the scope of the present paper, for further details the reader is referred to(4). The various processes which must be linked as part of an a priori methodology for relating emissions to air quality are shown in Figure 1. Source emissions, meteorology and chemical conversion processes are coupled together as part of the mathematical model which, in essence, describes the formation and transport of chemically-reacting species in the turbulent planetary boundary layer. Since routine solution of the equations describing urban scale atmospheric dynamics are not available most models are based on the species conservation equation, K-theory turbulence closure assumptions and the use of prescribed velocity fields. Pollutant concentration dynamics in the present work are represented by the atmospheric diffusion equation (ADE).

$$\frac{\partial c_i}{\partial t} + \nabla\cdot(\underline{u}c_i) = \nabla\cdot(K\cdot\nabla c_i) + R_i(c_1,\ldots,c_n,T) \qquad (1)$$

where c_i is the concentration of the species i, $\underline{u}$ is the carrier fluid velocity, with components [u,v,w], and K the second-order, turbulent diffusion tensor.

A model based on the solution of (1) will require several components:

(1) A kinetic mechanism describing the rates of atmospheric chemical reactions as a function of the concentration of the various species present.

(2) A source description, giving the temporal and spatial distribution of emissions from all significant pollutant sources within the airshed.

(3) A meteorological description, including wind speed and direction at each location in the airshed as a function of time, the vertical temperature structure and radiation intensity.

In current applications the chemical interactions, R_i, are described by the 50 step, lumped hydrocarbon, reaction mechanism of Falls and Seinfeld.[7] A detailed discussion of the formulation, validation and application of the model is presented in[8,9]. The remainder of the paper is devoted to a discussion of the major components of the model and applications to the design of air pollution control strategies.

3. COMPONENTS OF AN AIRSHED MODEL

The interaction of the various inputs and processes required to construct a mathematical description of atmospheric concentration dynamics is shown in Figure 1. Table 1 illustrates, in a simplified manner, the inputs actually needed to solve the atmospheric diffusion equation (ADE). Once the level of spatial, temporal and species resolution has been established together with the desired accuracy, then it is possible to consider the detailed preparation of the model inputs. From the standpoint of potential effects of errors in these inputs on the predictions of the model, joint consideration must be given to the level of

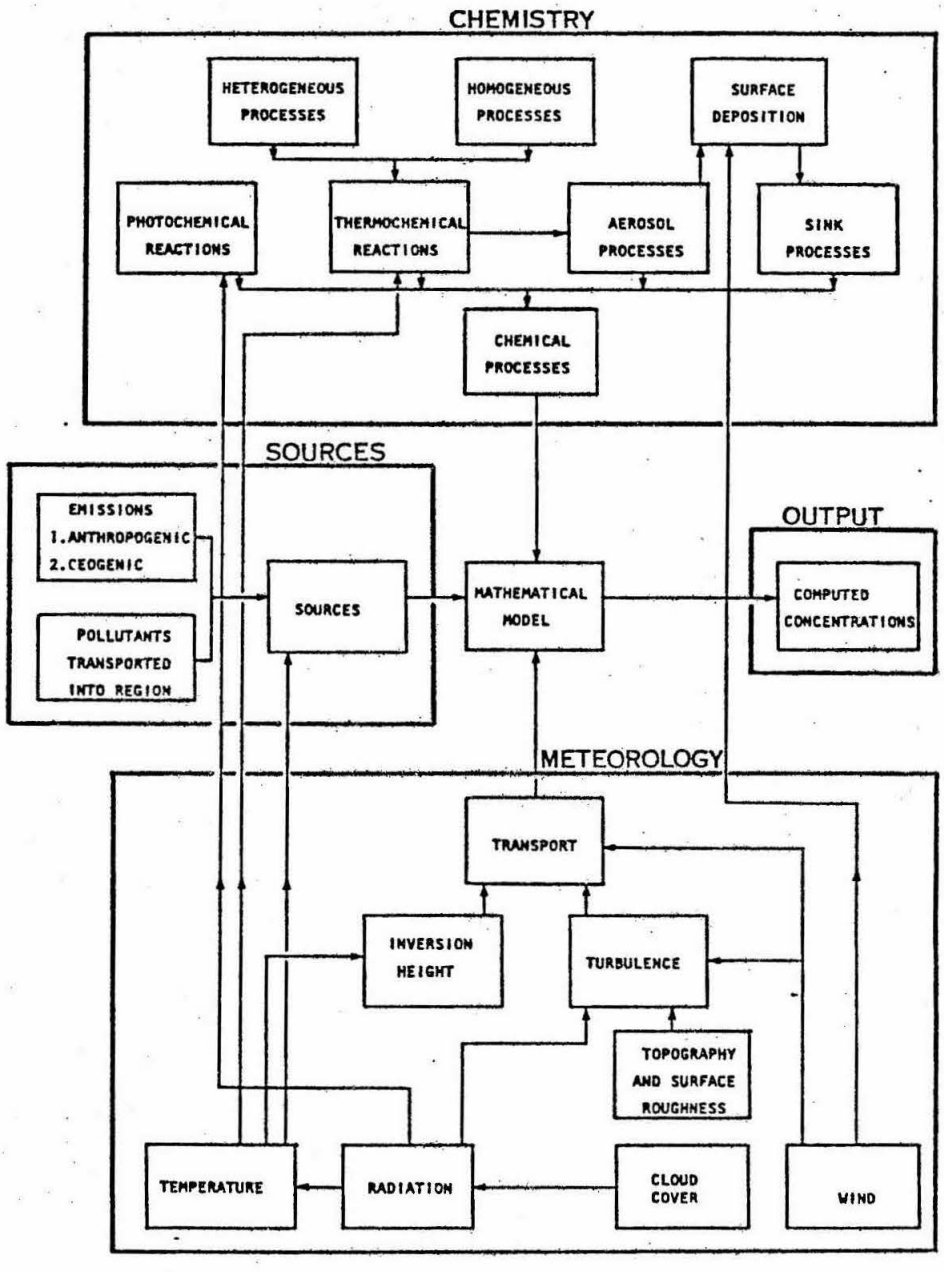

Figure 1. Simplified view of the factors involved in relating emissions to atmospheric air quality.

uncertainty and the sensitivity. The distinction between uncertainty and sensitivity has important implications for the resources allocated to data collection. For example, a parameter that has a large uncertainty but has little influence on the predictions of the ADE may not need extensive data preparation. A particularly promising technique for formal assessment of the effects of uncertainties in non-linear systems is the Fourier Amplitude Sensitivity Test (FAST) [8] which can determine which model variables most influence the predictions and consequently the level of accuracy required for the input parameters. The methodology has been successfully employed by Falls et al. [11] to evaluate the kinetic mechanism used in the present airshed model.

TABLE 1

Summary of Inputs Needed to Solve the Atmospheric Diffusion Equation

Basic Input	Detailed Components
Chemical Kinetics	Reaction Mechanism Rate Constants Ultraviolet Radiative Fluxes Deposition Velocities
Emission Inventory	Stationary Sources Mobile Sources
Meteorology	3-Dimensional Wind Field Mixing Depth Topography and Surface Roughness Turbulent Diffusion Coefficients Solar Insolation, U.V. Radiation Temperature Relative Humidity
Air Quality Data	Initial and Boundary Conditions Verification Data
Numerical Solution Procedure	Advective Transport Chemical Kinetics

4. CHEMICAL KINETICS

Photochemical air pollution is formed as a result of a complex interaction between sunlight and pollutant emissions. The development of a chemical mechanism which can be used to accurately describe the reactions occurring in an urban atmosphere is a difficult undertaking made even more complex by the presence, in most cases, of hundreds of hydrocarbon species. From a computational point of view it is not feasible to incorporate reaction pathways for each individual hydrocarbon and so chemical lumping procedures are used. Lumping is a process in which one or more reactants of similar structure and chemical reactivity are grouped together into a single class. The basic objective is to take advantage of the common features of the hydrocarbons and free radicals in order to minimize the number of species while at the same time maintaining a high degree of detail, in particular, with regard to the inorganic reactions. In the present airshed model the reaction mechanism contains six lumped hydrocarbon classes: ethylene, other olefins, alkanes, aromatics, formaldehyde and other aldehydes. The structure and interaction of the various species is shown in Figure 2. For details of the mechanism and its development the reader is referred to (7,8,11).

The hydrocarbon grouping enables the representation of a wide range of smog chamber experiments and atmospheric emissions. Initial testing and evaluation of the mechanisms was conducted against chamber studies. The results of a typical comparison against actual smog chamber data are shown in Figure 3. Such comparisons are especially important as they establish the validity of the mechanism and the chemical lumping procedures.

Once the mechanism has been validated then it can be used to develop oxidant isopleths. These diagrams indicate for particular atmospheric conditions the peak ozone levels given different initial concentrations of the precursor emissions, nitrogen oxides and reactive hydrocarbons. A schematic representation of a typical diagram is

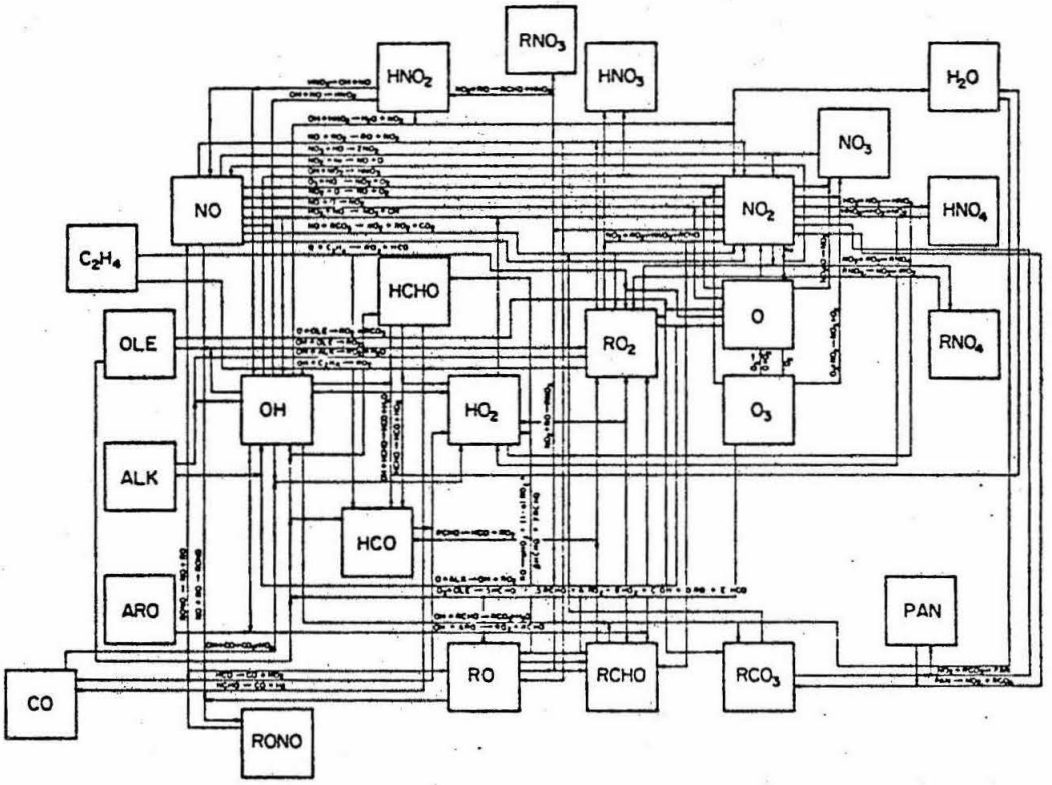

Figure 2. Structure and species interaction for a lumped Hydrocarbon model of photochemical air pollution chemistry.

is shown in Figure 4. The important point to note is that oxidant air quality is not linearly related to emissions. In fact it is possible to obtain

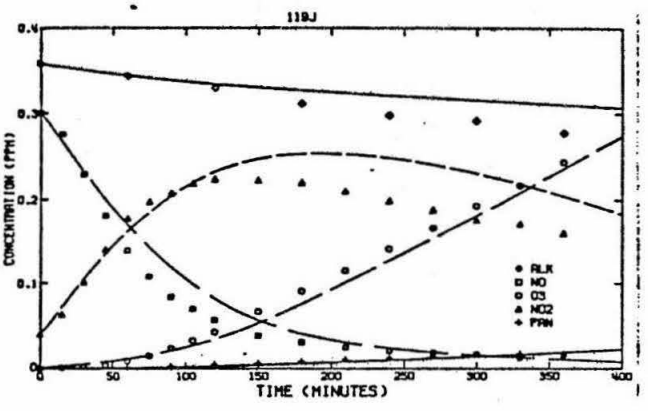

Figure 3. Results of a comparison of model predictions against smog chamber data from (12)

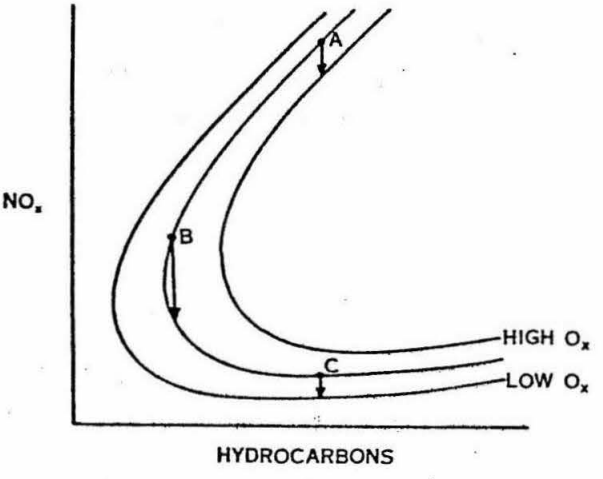

Figure 4. Oxidant Isopleths as a function of reactive hydrocarbons and nitrogen oxides

from a reduction in nitrogen oxides an increase, no change or decrease in oxidant levels depending on the starting conditions. It is results such as these which highlight the need for good oxidant prediction models. Unless the regulatory agency is very careful the historical practice of simply reducing emissions may not result in substantially improved air quality.

5. EMISSION INVENTORIES

Without a doubt the most important input to any airshed model is a comprehensive, detailed and accurate emission inventory. What is often neglected is that regardless of the approach used to relate emissions to ambient air quality it is almost impossible to design an efficient oxidant control strategy without an adequate inventory. When constructing an inventory it is necessary to assemble the source emission data at a level of accuracy consistent with the required spatial, temporal and chemical resolution of the problem.

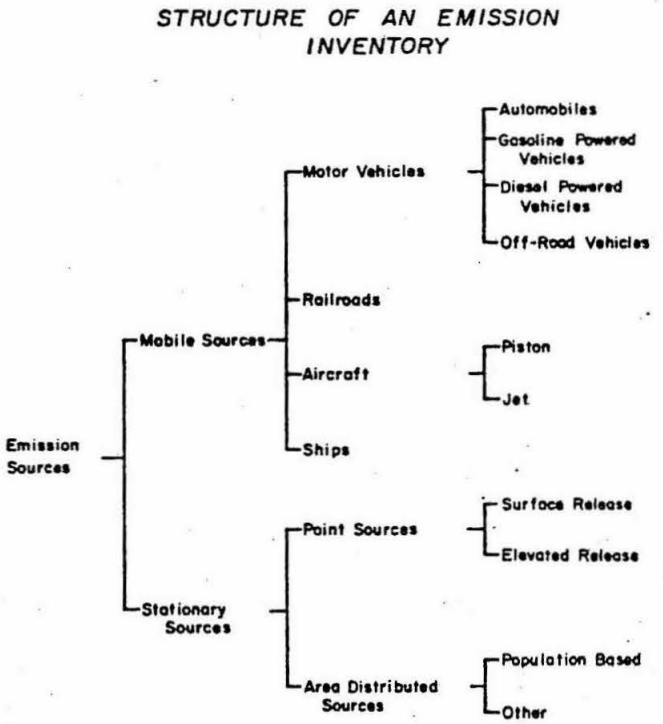

Figure 5. Simplified Structure of an Emissions Inventory.

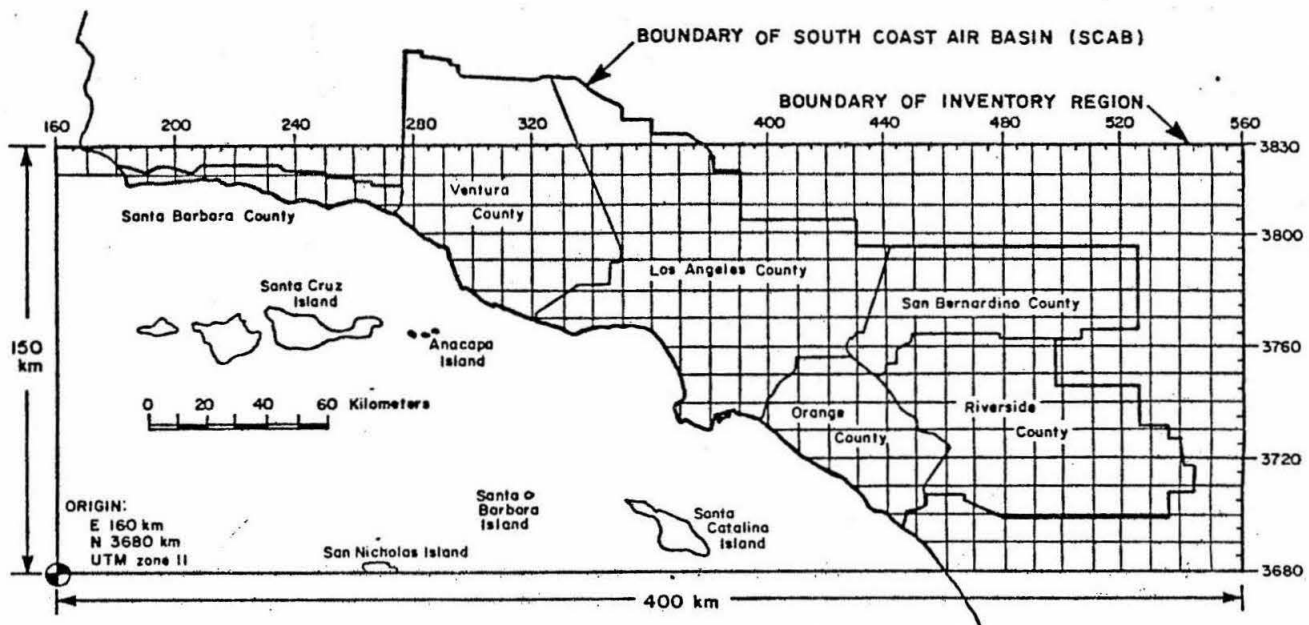

Figure 6. Boundary of the South Coast Air Basin (SCAB) of Southern California together with the grid system used to compile the emissions inventory.

By structuring the inventory in the manner shown in Figure 5 it is possible to vary, for example, the emissions from mobile sources and in fact from particular vehicle classes without altering the remainder of the inventory. While this structure is not required as part of the air quality calculation it considerably simplifies the task of constructing control strategies from a list of alternative emission control tactics. Once the structure has been established then it is possible to generate the emission distribution over the modeling region. As an illustration Figure 6 shows the South Coast Air Basin of California and the boundary of the region in which a source inventory has been complied. The grid shown is a ten kilometer grid, most calculations were carried out on the five kilometer grid as indicated by the small hash marks along the side of the grid. Figure 7 indicates a typical spatial and temporal distribution of reactive hydrocarbons within the airshed.

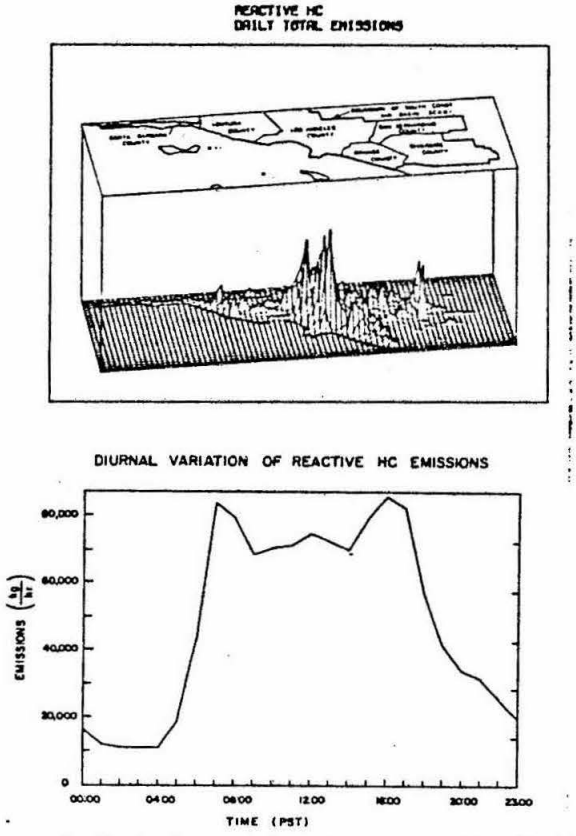

Figure 7. Typical spatial and temporal distribution of reactive hydrocarbon emissions in the South Coast Air Basin.

6. METEOROLOGY

Atmospheric transport and dispersion processes are important elements in an airshed model and they enter directly into the terms in the ADE. Wind speed and direction $\underline{u}$ appear directly in the governing equations, while the height through which the mixing occurs enters through the boundary conditions. The turbulent eddy diffusivities appear in (1) and also in the boundary conditions. Theoretical prediction of these quantities requires full solution of the turbulent atmospheric boundary-layer equation for conservation of momentum and energy. Because of the inherent difficulties objective analysis procedures are used to develop the fields from sparse and discrete observations. A complete discussion and presentation of the algorithms is given in (13,14). A typical example of a wind field generated from data available in the South Coast Air Basin is shown in Figure 8.

7. NUMERICAL SOLUTION OF THE ATMOSPHERIC DIFFUSION EQUATION

Complex numerical schemes are required for economic and accurate solution of the atmospheric diffusion equation (1). The wide variation in time scales, the nonlinearity of the chemistry and differences in transport processes considerably complicate the choice of numerical algorithms. In order to take advantage of the structure of the problem operator splitting techniques can be used. The basic idea is to write (1) in operator form (2) and then apply different, and specially suited, techniques to each component.

$$\frac{\partial c}{\partial t} + Lc = f \qquad (2)$$

The basic components of the problem are

$$\text{Transport} \quad \frac{\partial c}{\partial t} + Lc = 0 \qquad (3)$$

$$\text{Chemistry} \quad \frac{\partial c}{\partial t} = f \qquad (4)$$

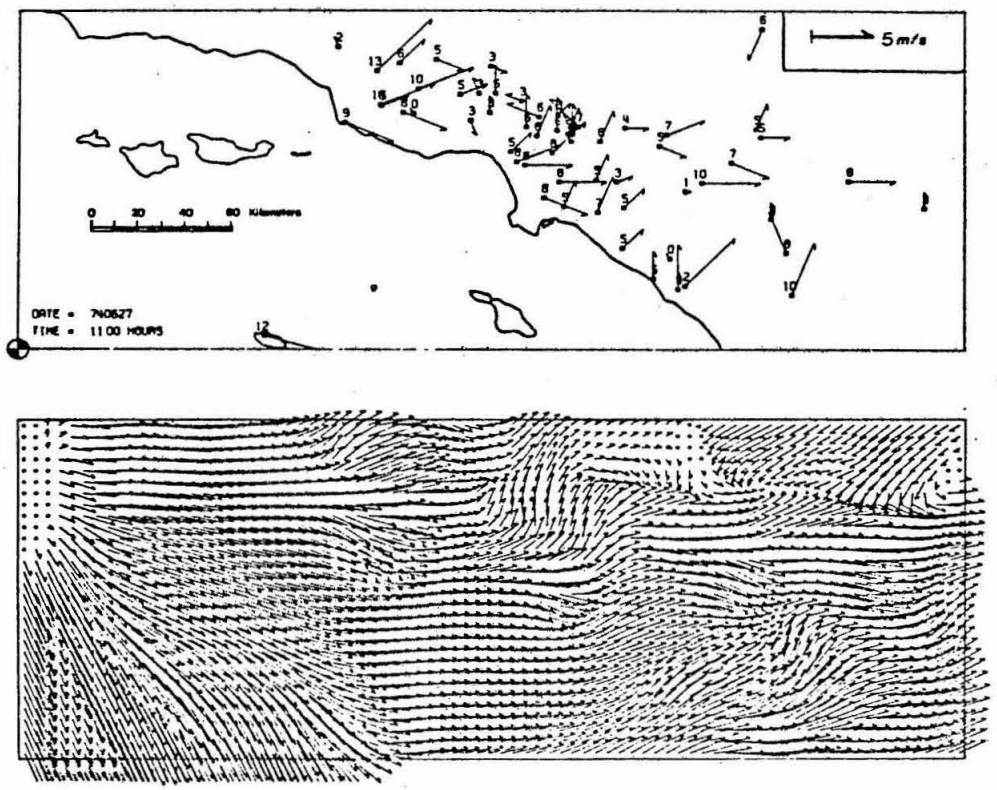

Figure 8. Horizontal Flow Field generated by an objective analysis procedure. (Length of the vector is proportional to wind speed).

If A_x, A_y, A_z, and A_c are the numerical approximations to the transport and chemical operators then a complete solution can be obtained from the sequence

$$c^{n+1} = A_x A_y A_z A_c (2\Delta t) A_z A_y A_x c^{n-1} \qquad (5)$$

where n is the time level and Δt the numerical time step. Each of the transport operators can be further split into advective and diffusive components. The methods employed for each of the transport and chemical operators are described in (8).

8. MODEL APPLICATIONS

Once the validity of the model has been established by careful comparison of the predictions against observations it can then be used with some confidence in practical decision making. Some typical applications are summarized in Table 2. In passing it is important to note some of the major advantages of employing models based on a description of atmospheric physics and chemistry.

(1) Complete spatial and temporal resolution is possible.

(2) Absolute quality prediction can be made.

(3) The model can be verified against atmospheric monitoring data.

While such models can often require substantial amounts of input data and computational resources their total implementation cost is miniscule compared to the economic expenditures associated with a typical control strategy.

TABLE 2

Some Typical Model Applications

Evaluation of the Air Quality Impact of Emission Control Strategies
Population Exposure Calculations
Siting of Monitoring Equipment
Emergency Episode Planning
Establishment of Emission Standards
Location Planning for New Sources
Air Quality Impacts of Alternative Energy Supplies
Land Use Planning

Instead of solving the atmospheric diffusion equation over the entire three-dimensional region, a grid-based model can be exercised in the trajectory format. Because of the simplicity of the trajectory approach it is an ideal way to illustrate the use of a model within the space limitations of this paper. A more detailed set of applications is described in (8).

The concept of a trajectory model is essentially that embodied in EKMA except that the actual emission inventory for the region is used to prescribe the inputs into the moving cell as a function of time. Therefore the trajectory model option of a three dimensional grid model produces absolute air quality predictions along a specific trajectory. Computational requirements for a trajectory model are obviously much smaller than those for a grid model and the predictions from a trajectory model calculation can be compared with air quality data for those stations that the trajectory passes. Although there are certain shortcomings to a trajectory model in terms of treatment of horizontal diffusion and vertical shear, the predictions from such a calculation are valuable in attempting to understand the air quality behavior along air trajectories. The equation governing the concentrations in a trajectory model is given by (6).

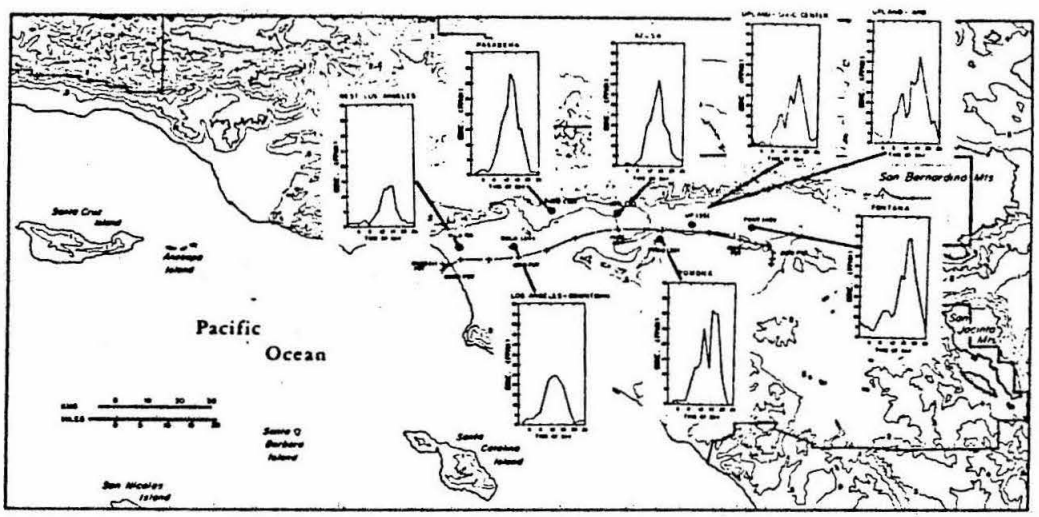

Figure 9. Typical trajectory path for June 27, 1974 and ozone concentration time histories at the closest monitoring sites.

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} K_{zz} \frac{\partial c_i}{\partial z} + R_i(c_1, \ldots, c_n, T) \qquad (6)$$

The basic difference between this equation and that in the EKMA model is the inclusion, in (6), of turbulent transport.

Using the meteorological and emission fields discussed in previous sections it is possible to calculate the path of an air parcel released anywhere in the South Coast Air Basin

Figure 9 shows a trajectory for June 27, 1974 and also the concentration versus time data for each station close to the trajectory. Figure 10 shows the calculated ground-level ozone concentration from the trajectory model using the Caltech model versus the concentrations at stations as the trajectory model passes those stations. This type of exercise, which must be carried out for a large number of trajectories and days, is the type used to estimate the accuracy of the model.

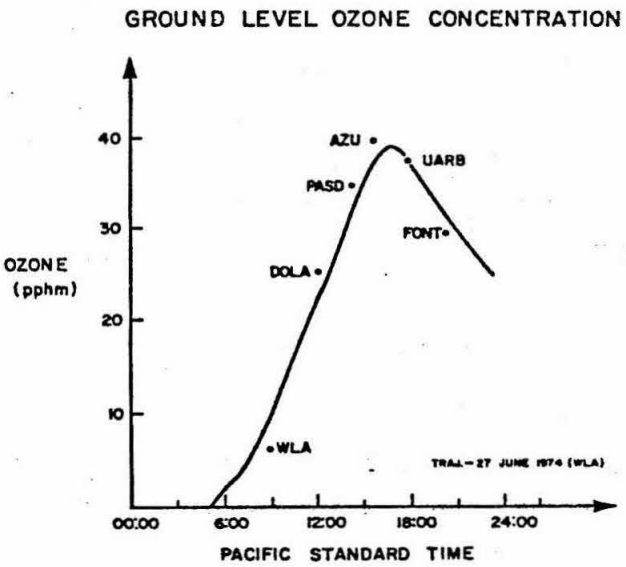

Figure 10. Predicted and observed ground level ozone concentration along the trajectories path shown in Figure 9.

The trajectory model can be exercised assuming various levels of hydrocarbon and NO_x control to produce isopleths of peak ozone levels as a function of percent reductions of the two precursors. Figure 11 shows such an isopleth plot. Table 3 then indicates the summary of the control levels for hydrocarbons and NO_x required to meet the 0.12 ppm Federal ambient air quality standard for ozone in the SCAB.

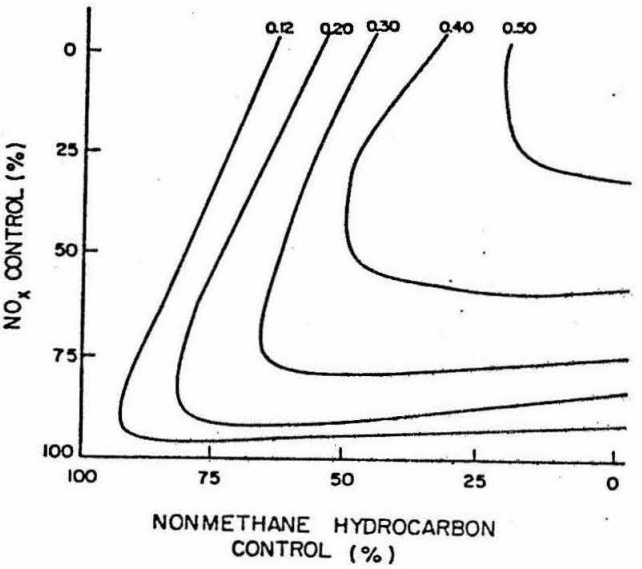

Figure 11. Ozone, isopleth plot corresponding to different levels of control for nonmethane hydrocarbons and nitrogen oxides. (Trajectory path from downtown Los Angeles to Upland 27 June 1974)

TABLE 3

Summary of Control Levels for Hydrocarbons and NO_x Required to Meet 0.12 ppm Federal Ozone Standard in SCAB

Modeling Method	% Control	
	RHC	NO_x*
Linear Rollback	83%	NA
EKMA HC/NO_x = 6.0	80%	38%
Trajectory Model	77%	38%

Design Value 0.51 ppmv O_3 27 June 1974

*Based on rollback of Federal annual average standard for NO_2.

9. CONCLUSION

This paper summarizes some elements of a mathematical model which can be used to describe the formation and transport of urban-scale photochemical air pollution.

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BIOGRAPHY

Mr. McRae is a research engineer in the Environmental Quality Laboratory at the California Institute of Technology. This paper summarizes some of his Ph.D. research work which is concerned with mathematical modeling of atmospheric processes. His other interests include application of such models to the design of control strategies for urban-scale air pollution, sensitivity analysis of non-linear systems, numerical analysis, aerosol formation processes and economic optimization.